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MECHANICAL PROPERTIES OF CROSSLINKED POLY(METHYL METHACRYLATE) POLYMERS UNDER SPACE ENVIRONMENTAL CONDITIONS

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I INTRODUCTION

This seventh Quarterly Technical Summary Report describes work conducted for the National Aeronautics and Space Administration under Task Order NASr-49(13) during the period, March 1 to May 31, 1965. The program is monitored by the Ames Research Center of NASA.

The objective of this study of crosslinked poly(methyl methacrylate) (PMMA) polymers is to obtain information on the behavior of crosslinked polymers in space environments. Of particular interest are the degradative changes in structure which take place *in vacuo* at elevated temperatures, the kinetics associated with the degradation process, and the influence of the degradative changes on the mechanical properties of the polymer.

During the report period, continuous and intermittent stress relaxation tests were carried out on several samples of crosslinked PMMA in vacuum, helium, and air, and some swelling experiments were made to complete the information reported in the previous Quarterly Technical Summary Report (Q.T.S.R. No. 6).

In anticipation of the procurement by the Ames Research Center of further samples with lower degrees of crosslinking, tensile testing was not continued during this period. It will be resumed when the new samples have been received from the Polycast Corporation; these will then be tested, together with lots No. 2, 3, 10, and 11, which have already been tested at 145, 165, and 185°C.

II STRESS RELAXATION

Additional continuous and intermittent stress relaxation tests were carried out on the more lightly crosslinked PMMA samples in air and in vacuum at elevated temperatures. In addition, runs were made in the vacuum apparatus (a) in helium, and (b) in vacuum, but in a glass jar instead of the normally used copper can, to obtain further information on the role of oxygen in the degradation process.

A. Atmospheric Tests

The results of the atmospheric tests described in Q.T.S.R. No. 6 showed that the degradation of crosslinked PMMA is relatively rapid in an atmospheric environment even at moderate temperatures (180-200°C). It also appeared that the stress decay became less rapid with increasing crosslink density, but the tests on which this conclusion is based were not made under properly comparable conditions. To study this effect further, and to ascertain if any differences existed between samples crosslinked with EDMA (ethylene glycol dimethacrylate) and with HDMA (hexamethylene glycol dimethacrylate), additional tests were carried out in the air relaxometer on Lots 2, 10, and 11 at 182°C. The results are plotted in Fig. 1, along with data for Lot 3 at 181°C, taken from Fig. 1 of Q.T.S.R. No. 6. All tests were made at a strain of about 10%, and both continuous and intermittent measurements were carried out on each sample. In every case the continuous and intermittent tests gave practically identical results, and thus the intermittent data are omitted for clarity.

Lots 3 and 11, and Lots 2 and 10, contain the same amount of crosslinker (EDMA for Lots 2 and 3, and HDMA for Lots 10 and 11). Figure 1 shows that the samples with the higher degree of crosslinking indeed degrade less rapidly than the more lightly crosslinked ones. However, these results are consistent with a rate of bond breakage which is

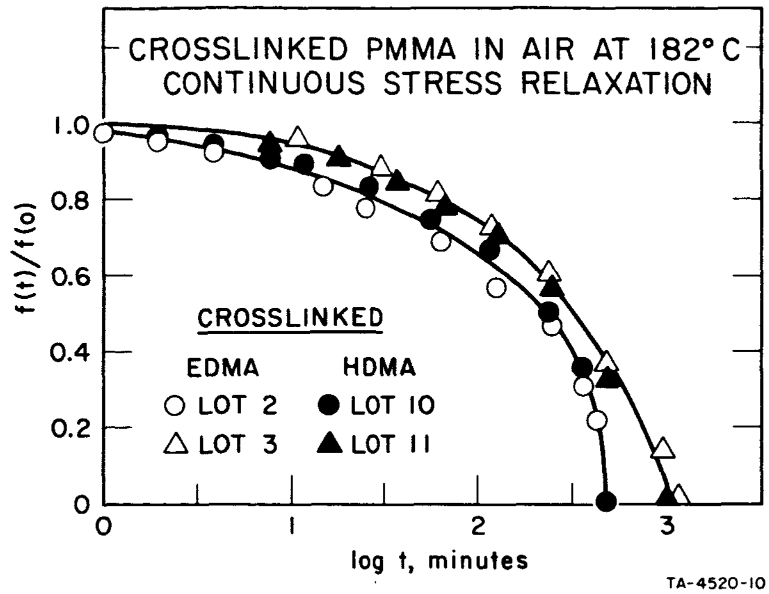

FIG. 1 CONTINUOUS STRESS RELAXATION OF CROSSLINKED PMMA IN AIR AT 182°C

independent of the degree of crosslinking. Figure 1 also shows that there are no significant differences between the degradation curves obtained on the EDMA-crosslinked and the HDMA-crosslinked samples at comparable degrees of crosslinking.

B. Tests Under Vacuum and in Helium

It was shown in Fig. of Q.T.S.R. No. 6 that vacuum has a considerable stabilizing influence on the thermal degradation of crosslinked PMMA. The effect of the vacuum is undoubtedly due to the reduced oxygen content of the environment. Because only a moderate vacuum (normally about 1 micron) can be achieved in the vacuum relaxometer, it was suggested that the copper can which surrounds the relaxometer may act as an oxygen getter. The considerable stability achieved in a moderate vacuum could then be explained by considering that the partial pressure of oxygen near the specimen may be far lower than that calculated by assuming the residual gas in the chamber to be air, because of scavenging of oxygen by the copper vacuum housing at the elevated temperatures employed.

A run was made therefore on Lot 2 at 187°C in a glass jar. The result is compared in Fig. 2 with a run in the copper can at 227°C. The

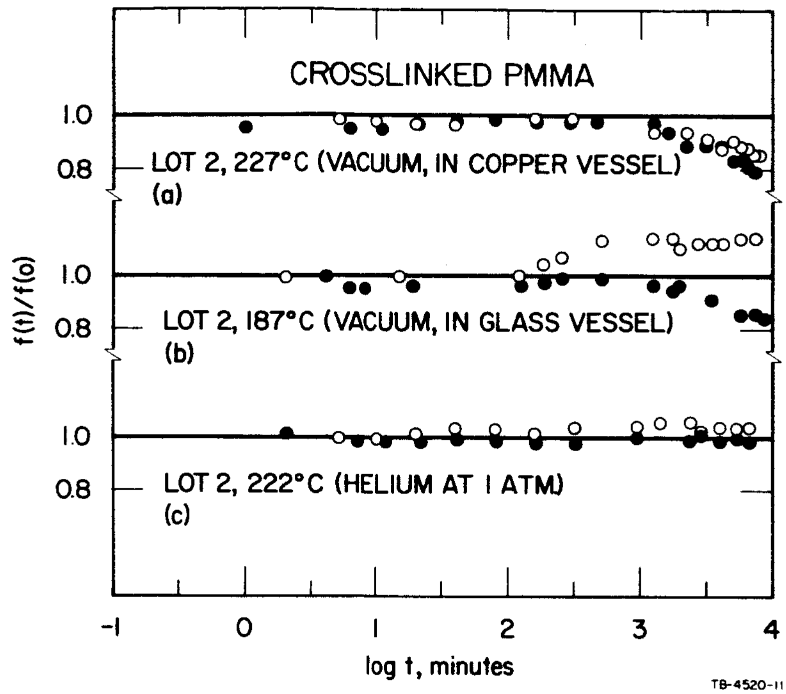

FIG. 2 CONTINUOUS AND INTERMITTENT STRESS RELAXATION OF CROSSLINKED PMMA (a) IN VACUUM IN COPPER JAR, (b) IN VACUUM IN GLASS JAR, AND (c) IN HELIUM

two runs show no significantly different features. No appreciable degradation is observed in either case until after 1000 minutes, when both tests show slight stress decay. An increase of force with time is observed for the intermittent measurements in the glass jar, but this seems to be characteristic for runs at lower temperatures. (See data for Lots 1 and 3, Figs. 2 and 3 of Q.T.S.R. No. 6.)

Another possible explanation for the stability under vacuum is that some material which catalyzes degradation is degassed while specimens are being brought to run temperature under vacuum. To test this possibility, a run was made under helium at about one atmosphere. After installation of the samples, the chamber was evacuated and filled with helium, and this procedure was repeated three times. (The brief exposure of the samples to vacuum at room temperature, far below T_g, was not expected to cause any appreciable outgassing.) The chamber was then immersed in the thermostatted bath at 222°C, and the run was continued in the usual manner, while a slight positive pressure of helium was maintained by a mercury manostat. As shown in Fig. 2, there was no appreciable stress decay during the entire run (about 110 hours), and it must be concluded that the increased stability is not due to the removal of a catalyst by outgassing.

Since little degradation in vacuum was observed at temperatures up to about 225°C, an attempt was made to speed up the rate of stress decay by raising the temperature as high as possible. Continuous and intermittent tests in vacuum at 246°C were carried out on specimens of Lots 2, 3, 10, and 11. The results for Lots 2 and 10, the most lightly crosslinked samples available, are shown in Fig. 3. Although at this temperature some degradation occurs in a period of several hours, tests were cut short by breakage of both the continuous and intermittent specimens.

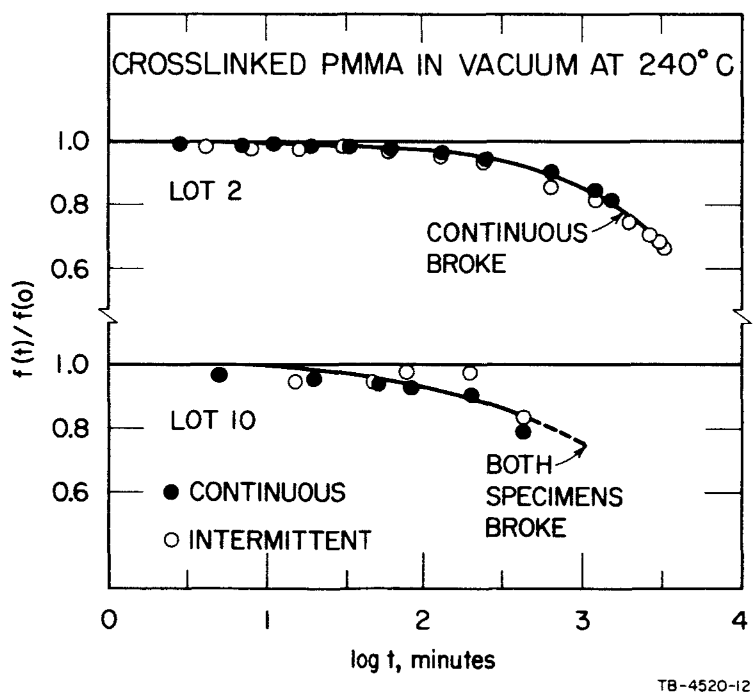

FIG. 3 CONTINUOUS AND INTERMITTENT STRESS RELAXATION OF CROSSLINKED PMMA IN VACUUM AT 246°C

Tests performed at the same temperature on Lots 3 and 11, which are more highly crosslinked, were ended by breakage of the specimen within 2-3 hours, before appreciable degradation occurred.

A further attempt was made to observe degradation in Lots 2 and 10 by aging the samples at 246° in an unstressed state for about 45 hours before beginning the tests. Both samples broke within 10 minutes after being extended.

C. Conclusions

The experiments carried out so far have demonstrated that:

1. Stress decay in crosslinked PMMA is quite rapid in an atmospheric environment even at moderate temperatures (180-200°C), with no observable difference between the rate of stress decay in continuously and intermittently stressed samples. The decay is slower for more highly crosslinked samples, but there is little difference between results for samples crosslinked to equivalent degrees with EDMA and HDMA.

2. Stress decay of the same materials in moderate vacuum (approximately 1 μ) is very slow compared with results obtained in air, despite appreciable weight losses. However, the specimens show a tendency to break which increases with temperature and strain, and with the degree of crosslinking. This prevents the determination of stress decay curves over an extended range.

Even at the moderate vacuum attainable in the vacuum relaxometer, the increase in stability is so great, that no appreciable degradation occurs in the currently available samples up to about 250°C. At this temperature, degradation becomes apparent in the two most lightly crosslinked samples just before they break. A further increase in temperature at the currently employed strain level of about 10% is useless since it only leads to rupture of the specimens before any degradation can be observed. At the same time the current strain level of almost 10% is already near the lower limit of practicability for stress relaxation studies.

Samples with lower degrees of crosslinking are being procured from Polycast Corporation by the Ames Research Center. It is hoped that these samples will allow determination of a sufficiently large portion of the stress decay curves so that an analysis of the kinetics of the process can be attempted.

In addition, some information on the possible effect of vacuum on the break properties of crosslinked PMMA samples will be sought during the next report period.

III SWELLING MEASUREMENTS

Swelling measurements, as described in Q.T.S.R. No. 6, were made on Lot 10, which was not available then.

Since swelling measurements in chloroform on Lot 3 had previously been made after refluxing the sample for 24 hours in n-butyl acetate, these measurements were repeated with the same one-hour refluxing period to which all other samples had been subjected.

The results are shown in Table I.

Table I

SWELLING MEASUREMENTS ON CROSSLINKED PMMA

Lot No.	Cross-linker	Amount of Crosslinker % w/w	Gel Fraction from Swelling		Moles of Network Chains per cc x 10^4		
					From Swelling		From Amount of Crosslinker
			$(CH_2Cl)_2$	$CHCl_3$	$(CH_2Cl)_2$	$CHCl_3$	
2	EDMA	0.25	0.94	0.83	2.21	1.48	0.30
3	EDMA	1.0	0.94	0.98	4.54	4.83	1.2
4	EDMA	6.0	0.94	0.91	9.57	7.59	7.15
5	EDMA	16.0	0.96	0.96	33.8	26.1	19.2
10	HDMA	0.25	0.95	0.96	1.85	2.01	0.23
11	HDMA	1.0	0.90	0.91	3.07	2.59	0.93
12	HDMA	6.0	0.95	0.95	17.1	13.3	5.55

This table amends Table II of Quarterly Technical Summary Report No. 6.